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ABIOTIC OXYGEN-DOMINATED ATMOSPHERES ON TERRESTRIAL HABITABLE ZONE PLANETS

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ABSTRACT

Detection of life on other planets requires identification of biosignatures, i.e., observable planetary properties that robustly indicate the presence of a biosphere. One of the most widely accepted biosignatures for an Earth-like planet is an atmosphere where oxygen is a major constituent. Here we show that lifeless habitable zone terrestrial planets around any star type may develop oxygen-dominated atmospheres as a result of water photolysis, because the cold trap mechanism that protects H₂O on Earth is ineffective when the atmospheric inventory of non-condensing gases (e.g., N₂, Ar) is low. Hence the spectral features of O₂ and O₃ alone cannot be regarded as robust signs of extraterrestrial life.

1. INTRODUCTION

The rapid growth of exoplanet discovery and characterization over the last two decades has fueled hopes that in the relatively near future, we may be able to observe the atmospheres of Earth-like planets spectroscopically. Such targets will be intrinsically interesting for comparative planetology, but also for the major reason that they may host life. To search for life on exoplanets by observing their atmospheres, we must first decide on spectral features that can be used as biosignatures. Despite extensive theoretical study of various possibilities, detections of molecular oxygen (O₂) and its photochemical byproduct, ozone (O₃), are still generally regarded as important potential indicators of Earth-like life on another planet (Segura et al. 2005; Kaltenegger et al. 2010; Snellen et al. 2013; Kasting et al. 2013).

Various authors have investigated the idea that abiotic oxygen production could lead to ‘false positives’ for life (Selsis et al. 2002; Segura et al. 2007; Léger et al. 2011; Hu et al. 2012; Tian et al. 2014). For example, it has recently been argued that the build-up of O₂ to levels of $\sim 2 - 3 \times 10^{-3}$ molar concentration in CO₂-rich atmospheres could occur for planets around M-class stars, because of the elevated XUV/NUV ratios in these cases (Tian et al. 2014). Extensive atmospheric O₂ buildup due to H₂O photolysis followed by H escape may also occur on planets that enter a runaway greenhouse state (Ingersoll 1969; Kasting 1988; Leconte et al. 2013). However, because by definition the runaway greenhouse only occurs on planets inside the inner edge of the habitable zone, it should not lead to identification of false positives for life.

For planets inside the habitable zone, it is commonly believed that H₂O photolysis will always be strongly limited by cold-trapping of water vapour in the lower atmosphere. The purpose of this note is to point out that a mechanism for O₂ build-up to levels where it is the *dominant* atmospheric gas exists for terrestrial¹ planets in the

habitable zone around any star type. The reason for this is that the extent of H₂O cold-trapping depends strongly on the amount of non-condensable gas in the atmosphere.

2. DEPENDENCE OF THE COLD TRAP ON THE NON-CONDENSIBLE GAS INVENTORY

Previously, we have shown that the degree to which a condensing gas such as H₂O is transported to a planet’s upper atmosphere is determined primarily by the dimensionless number $\mathcal{M} = \epsilon p_v L / p_n c_p T_s$, where L is the specific latent heat of the condensing gas, c_p is the specific heat capacity at constant pressure of the non-condensing gas (or gas mixture), T_s is temperature, p_v and p_n are respectively the partial pressures of the condensing and non-condensing gases in the atmosphere, $\epsilon = m_v/m_n$ is the molar mass ratio between the two gases, and all values are defined at the surface. \mathcal{M} is essentially the ratio of the latent heat of the condensing gas (here, H₂O) to the sensible heat of the non-condensing gas (primarily N₂ on Earth) (Wordsworth and Pierrehumbert 2013). Values of $\mathcal{M} > 1$ ($\mathcal{M} < 1$) correspond in general to situations where the upper atmosphere is moist (dry).

Figure 1 shows the surface temperature dividing the moist and dry upper atmosphere regimes as a function of p_n for a pure N₂–H₂O mixture. As can be seen, on a planet with 1 bar of N₂, a surface temperature of > 340 K is required for a moist upper atmosphere, in rough agreement with detailed radiative-convective calculations (Wordsworth and Pierrehumbert 2013). However, the required surface temperature is a strong function of p_n . For 0.1 bar only ~ 295 K is required, while for 0.01 bar the value drops to ~ 255 K. In general there is no reason to expect that Earth’s atmospheric nitrogen inventory is typical for a rocky planet: in the inner Solar System alone, the range of atmospheric N₂ as a function of planetary mass spans 3.3 times (Venus) to 6.6×10^{-4} times (Mars) that of Earth. Delivery and removal of volatiles on terrestrial planets is dependent on an array of complex, chaotic processes, so wide variations in inventories should be expected (Raymond et al. 2006; Lichtenegger et al. 2010; Lammer et al. 2009).

¹ Here we define ‘terrestrial’ in the standard (broad) way as describing any planet of low enough mass that it does not possess a dense hydrogen envelope.

3. ABIOTIC OXYGEN ON PLANETS WITH PURE H₂O ATMOSPHERES

The O₂ buildup mechanism can easily be understood intuitively by a thought experiment involving a hypothetical planet with a pure H₂O composition (Figure 2). Lacking atmospheric N₂, Ar and CO₂, such a planet will initially have a pure H₂O atmosphere, with the surface pressure determined by the Clausius-Clayperon relation (Andrews 2010; Pierrehumbert 2011). If the planet has the same orbit and incident stellar flux as present-day Earth, it will most likely be in a snowball state (Budyko 1969). However, because H₂O cannot be cold-trapped when it is the only gas in the atmosphere, it will be photolysed by XUV and UV radiation from the host star (primarily via $\text{H}_2\text{O} + h\nu \rightarrow \text{OH}^* + \text{H}^*$). The resultant atomic hydrogen will escape to space at a rate dependent on factors such as the XUV energy input and the temperature of the thermosphere, and hence the atmosphere will oxidise².

In the 1D limit with no surface mass fluxes, atmospheric O₂ will build up on such a planet until p_n is high enough to cold-trap H₂O and reduce loss rates to negligible values. In 3D, the initial atmospheric evolution may depend on the planet's orbit and sub-surface heat flux / transport rate, because on a tidally locked, ice-covered planet with pure H₂O atmosphere, conditions on the dark side could be so cold that even O₂ would condense. However, on a planet with Earth-like rotation and obliquity, all regions of the planet receive starlight at some point in the year, so once the surface O₂ inventory passed a given threshold, buildup of an O₂ atmosphere would likely be inevitable. In addition, for any planet, transient heating events such as meteorite impacts would be able to force transitions to a stable state of high atmospheric pressure³.

What about more general scenarios? First, we can relax the assumption of zero downward flux at the surface and consider cases where the created O₂ can be used to oxidise the interior. Then, redox balance dictates that atmospheric oxygen levels must build up until the loss of hydrogen to space is balanced by the surface removal rate of oxidising material. For example, if an O₂ removal rate⁴ of 5×10^9 molecules cm⁻² s⁻¹ at the surface is balanced by diffusion-limited H₂O loss, given an escape rate $\Phi = b_{\text{H}_2\text{O}-\text{O}_2} f_{\text{H}_2\text{O}} (H_{\text{O}_2}^{-1} - H_{\text{H}_2\text{O}}^{-1})$, the molar concentration of H₂O at the cold trap⁵ must be 3×10^{-3} mol/mol under Earth gravity. Here $b_{\text{H}_2\text{O}-\text{O}_2}$ is the binary diffu-

sion coefficient of H₂O in O₂ (Marrero and Mason 1972), H_{O_2} and $H_{\text{H}_2\text{O}}$ are respectively the atmospheric scale heights of O₂ and H₂O, and $f_{\text{H}_2\text{O}}$ is the cold trap H₂O molar concentration.

The surface O₂ partial pressure required to match this cold-trap concentration, which can be calculated by integrating the moist adiabat equation (Ingersoll 1969) as in Wordsworth and Pierrehumbert (2013), depends on both the surface and cold-trap temperatures. In Earth's present-day oxygen-rich atmosphere, the cold trap occurs at a relatively high $T_t \sim 210$ K, due primarily to the warming effect of ultraviolet solar absorption by O₃ (Andrews 2010). Given $T_s = 288$ K and $T_t = 210$ K, $f_{\text{H}_2\text{O}} = 3 \times 10^{-3}$ mol/mol requires a surface O₂ partial pressure of 0.15 bar. For a snowball planet with $T_s = 240$ K, this would drop to 0.022 bar. By comparison, for $T_s = 288$ K and $T_t = 140$ K, 0.025 bars is required⁶. Because O₂ build-up should lead to O₃ formation and hence stratospheric heating, O₂ partial pressures of at least a fraction of a bar appear plausible once the planet's atmosphere reaches a steady state.

4. ABIOTIC OXYGEN ON EARTH-LIKE PLANETS

How would things change on a more complex planet where other atmospheric constituents were present? First, if the atmosphere contains some N₂ or Ar, the amount of O₂ required to block H₂O escape will clearly be decreased, and increased horizontal heat transport would reduce the likelihood of atmospheric bistability via O₂ condensation in the planet's regions of low surface instellation. Reduced gases such as methane, which can be outgassed from a planet's interior by abiotic processes (Levi et al. 2013; Guzmán-Marmolejo et al. 2013), could have lifetimes similar to those on Earth today in an O₂-rich atmosphere, although variations in O₃ and NO_x concentrations as a function of UV levels and atmospheric composition might alter this (Wayne 2000). In addition, volcanically emitted sulphur species and heterogeneous chemistry will also affect the atmospheric redox balance. Future investigations using photochemistry models will allow constraints on the importance of these effects as a function of the water loss rate.

Surface/interior redox exchanges are another source of complexity on a low-N₂ Earth-like planet. If the planet forms with a hydrogen envelope that is lost to space early on (e.g., Genda and Ikoma 2008), its crust and oceans should initially be reducing, and the oxidised products of H₂O photolysis might react rapidly with the surface at first. However, as long as this occurred, the upper atmosphere would remain H₂O-rich and rapid photolysis could continue. Over time, the planetary surface and interior would become oxidised, decreasing their ability to act as an oxygen sink. Assuming Earth's present-day XUV flux, a lower limit on H₂ escape from a hydrogen-rich homopause is $\sim 4 \times 10^{10}$ molecules cm⁻² s⁻¹ (Tian et al. 2005). Given this, an N₂-poor Earth could lose 2.1×10^{22} moles of H₂O over 4 Gy, or 28% of the current ocean volume⁷. This translates to 66.2 bar of

² We assume here, as in previous work, that the efficiency of H₂O photolysis is not a limiting factor on the rate of hydrogen escape.

³ The latent heat of sublimation of O₂ ($L_{\text{O}_2} = 213$ kJ kg⁻¹) is only around 1/10th that of H₂O (Lide 2000). Hence with only 25% energy conversion efficiency, the kinetic energy of an impactor travelling at 10 km s⁻¹ with density 3 g cm⁻³ would be sufficient to sublimate a 1-bar atmosphere of O₂ on an Earth-size planet if its radius was 19.2 km.

⁴ The actual rate of interior oxidation of an H₂O world with an oxygen-rich atmosphere is difficult to calculate. For comparison, the average rate of oxidation due to Fe³⁺ subduction to the mantle on Earth over the last 4 Gy was estimated as $1.9 - 7.1 \times 10^9$ molecules O₂ cm⁻² s⁻¹ in Catling et al. (2001).

⁵ The relationship between Φ and $f_{\text{H}_2\text{O}}$ depends weakly on the homopause temperature T_h via the scale heights and $b_{\text{H}_2\text{O}-\text{O}_2}$. For simplicity, $T_h = 300$ K is used here.

⁶ The $T_t = 140$ K calculation may underestimate the required surface O₂ partial pressure, because effective blocking of H₂O photolysis also requires the cold-trap altitude to be lower than that at which the atmospheric opacity in the UV becomes less than unity.

⁷ In this calculation, we assume that 50% of the escaping hydro-

atmospheric O₂ – a large enough quantity to cause significant irreversible oxidation of the solid planet and hence a strong decrease in the reducing power of the surface. Because XUV fluxes are greatly enhanced around young dwarf stars in general, total water loss could be many times this value in many cases (Ribas et al. 2005; Ribas et al. 2010; Linsky et al. 2014).

Finally, an Earth-like planet could have CO₂ outgassing, plate tectonics and hence the potential for a carbonate-silicate weathering feedback (Walker et al. 1981). The CO₂ cycle on an initially anoxic planet without N₂ or Ar would be complex, because CO₂ condenses at relatively high temperatures (Lide 2000) but has low compressive strength in solid form (Clark and Mullin 1976). In the absence of ocean/interior heat transport processes, outgassed CO₂ could build up on the low installation regions of a planet until the return flow of CO₂ glaciers became sufficient to transport it back to high installation regions.

Setting aside the complexity of the full climate problem for future study, we can nonetheless demonstrate the potential for O₂ build-up in cases where CO₂ levels are such that the planet has an Earth-like global mean surface temperature. Figure 3 shows the variation of atmospheric temperature and H₂O molar concentration with atmospheric N₂ content calculated using the same methodology as in Wordsworth and Pierrehumbert (2013), for an Earth-like planet at 1 AU around a Sun-like star, assuming an N₂–CO₂–H₂O atmosphere with tropospheric H₂O relative humidity of 0.5. In each case, the CO₂ molar concentration has been chosen to yield close to $T_s = 288$ K in equilibrium. As can be seen, once the N₂ content drops below a few percent of that on present-day Earth, the high atmosphere becomes rich in H₂O, implying rapid photolysis and hence planetary oxidation. Hence we may conclude that even planets that are Earth-like in all respects except for the N₂ content of their atmospheres have the potential to build up O₂

abiotically until it is a major atmospheric constituent.

5. CONCLUSION

Because O₂ can become the dominant gas in the atmosphere of a lifeless planet, alone it cannot be regarded as a robust biosignature. Our results do not necessarily rule out its utility in every case. However, they do demonstrate that the situation is considerably more complex than has previously been believed, with the likelihood of an abiotic O₂-rich atmosphere emerging a complicated function of a planet’s accretion history, internal chemistry, atmospheric dynamics and orbital state. Investigation of the range of possibilities for terrestrial planets with variable N₂ and noble gas inventories should be a rich area for future theoretical research that will help to expand our understanding of climate evolution mechanisms. Nonetheless, for a specific exoplanet, even detailed modelling might not lead to a definite conclusion given the inherent uncertainties in processes such as volatile delivery during formation.

Observationally, there may still be a way to distinguish the scenarios we discuss here, but only if a reliable way is developed to retrieve the ratio of O₂ to N₂ or Ar in an exoplanet’s atmosphere. In principle this may be achieved by analysis of the planet’s spectrally resolved phase curve (Selsis et al. 2011), or in transit by measurement of the spectral Rayleigh scattering slope (Benneke and Seager 2012) in a clear-sky (i.e., aerosol-free) atmosphere, or possibly via spectroscopic observation of oxygen dimer features (Misra et al. 2014). More work will be required to assess the potential of these techniques to determine O₂/N₂ mixing ratios in realistic planetary atmospheres.

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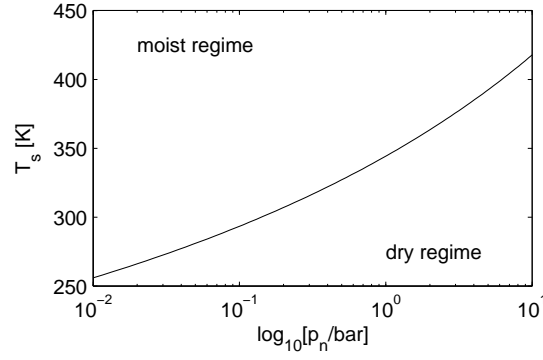


FIG. 1.— Surface temperature defining the transition between moist and dry upper atmosphere regimes as a function of the surface partial pressure of the non-condensable atmospheric component. Here, the non-condensing and condensing gases are N_2 and H_2O , respectively. Results using O_2 , Ar or CO_2 as the non-condensing gas are similar.

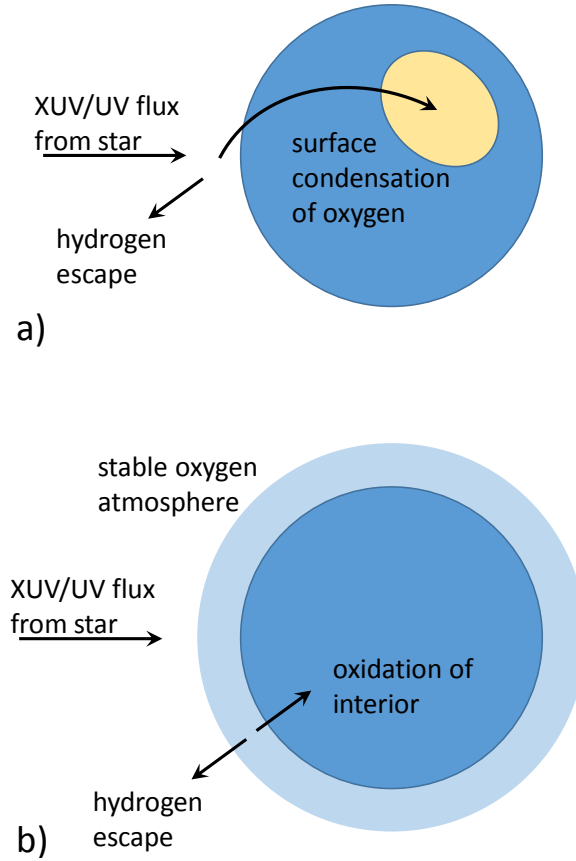


FIG. 2.— Schematic of possible evolutionary pathways for an initially water-dominated planet exposed to stellar XUV and UV. a) H_2O photolysis causes O_2 and other oxidised products to build up on the planet's surface regions of low net instellation. b) Once sufficient O_2 has built up, the planet can transition to a state where a stable O_2 atmosphere is present and hydrogen escape to space is balanced by oxidation of the interior.

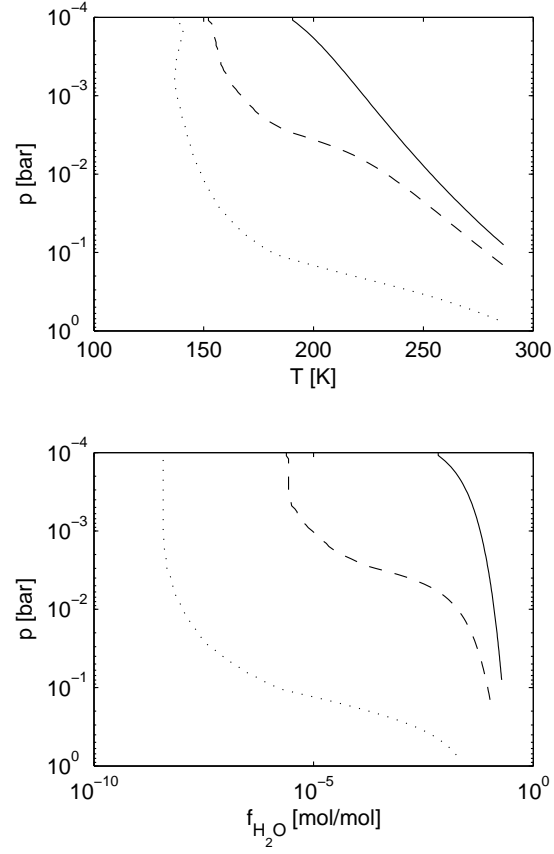


FIG. 3.— Atmospheric a) temperature and b) H_2O molar concentration in thermal equilibrium as a function of pressure, as simulated by the 1D radiative-convective model. In each case the atmospheric composition is $\text{N}_2\text{--CO}_2\text{--H}_2\text{O}$. For the dotted, dashed and solid lines, the N_2 inventories are 1, 0.17 and 0.007 times that of present-day Earth, and the dry CO_2 molar concentration is 1×10^{-3} , 0.1 and 0.9 mol/mol, respectively. As can be seen, the upper atmosphere is moist when N_2 levels are low, implying rapid H_2O photolysis.